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# ***In Situ* Transmission Electron Microscopy Observations of Rapid Solidification of Aluminum Thin Films**

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Using high time resolution transmission electron microscopy we have observed rapid solidification dynamics in pulsed laser melted 80 nm thick Al thin films. The nanometer spatial and 15 nanosecond temporal resolution of the dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory allowed us to study the morphology and dynamics of the moving transformation front during rapid solidification. Additionally, we used an automated orientation imaging system in the TEM to post mortem analyze grain orientations of the solidified microstructure near the position of the solid liquid interface at the start of solidification.

Corrosion behavior, mechanical, electrical and many other materials properties critically depend on the microstructure of materials and its scale. The understanding of microstructural evolution during processing steps such as solidification is of great scientific and technological importance. Metal thin films are widely used in many applications, such as microelectronics, where the control of structure-sensitive properties is of great importance [1,2]. Previous investigations [3,4] reported that single-shot laser melting of thin metal films on Si substrates and the subsequent ultra rapid solidification yield unique microstructures with high aspect ratio grains, up to 50  $\mu\text{m}$  in length and about 1 – 2  $\mu\text{m}$  in width, which exhibit a strong growth texture. Computational modeling of laser melting and rapid solidification predicts extremely large heating and cooling rates ( $\sim 10^8 - 10^{10}$  K/m) and very short duration for the entire process,  $\sim 150 - 200$  ns. Much is still unknown about the details of the thermodynamics and kinetics of the processes that govern the laser induced rapid solidification in metal thin films and lead to the formation of extraordinary microstructures. For metals near the melting point the optical properties of liquid and solid are very similar. Hence, optical methods that facilitated measurement of rapid solidification kinetics in Si [5] are much more difficult to apply to metals. While theoretical models are in place, virtually no experimental data exist to validate computational predictions of the kinetics of the process and the structure of the liquid solid interface in the case of metal thin films.

In this study we performed an in-situ investigation of rapid solidification in polycrystalline aluminum thin films using the dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory [6]. The unprecedented 15 ns time and nm spatial resolution of the DTEM [7,8] revealed the details of the rapidly propagating solidification interfaces and the solidified microstructure. The samples comprised 80 nm thick Al thin films sputter-deposited on TEM grids with 100 nm thick  $\text{Si}_3\text{N}_4$  windows. The

DTEM experiments were performed by, first, melting the Al films inside the DTEM with a single laser pulse of 12 ns FWHM at a 45° angle (YAG laser with wavelength 1064 nm) thereby creating an elliptically shaped melt pool. After a pre-selected time delay, a single electron pulse, emitted from a laser driven photocathode, illuminates this molten area to acquire either an image or diffraction data.

Figure 1 shows a series of images, diffraction patterns (DP) and corresponding radial averaged intensity (RAI) vs. reciprocal lattice spacing ( $\text{nm}^{-1}$ ) plots for different time delays. RAI plots can be interpreted similarly to x-ray diffraction plots, including information about crystallography, texturing, and pair distribution functions in amorphous and liquid materials.

Before melting, the image of the as-deposited nanocrystalline thin film shows little contrast due to the low magnification,  $\sim 4000\times$ , and the fine,  $\sim 50\text{ nm}$ , grain size (Fig. 1a). The corresponding DP shows a ring pattern characteristic of the nanocrystalline Al film superimposed on the diffuse background from the amorphous  $\text{Si}_3\text{N}_4$  substrate, as identified by the diffuse peaks situated underneath sharper Al diffraction maxima in the RAI plot. After heating the sample with a 12 ns laser pulse to fluences of  $\sim 510\text{ mJ cm}^{-2}$ , the Al layer melts, as indicated by disappearance of the nanocrystalline grains in the bright field (BF) image and the rings in the DP. In the corresponding RAI the sharp Al peaks disappear, while the diffuse maxima broaden (Fig. 1b). The pattern in the RAI plot could be fitted assuming the presence of two different amorphous phases, liquid Al and amorphous  $\text{Si}_3\text{N}_4$ . After 5  $\mu\text{s}$ , the solidification front came into the field of view, exhibiting a distinctly smooth morphology free from local protrusions that would suggest growth of thermal dendrites. Although, the liquid-solid interface is curved on the micron length scale, its smooth character at length scales on the order of the film thickness (80nm) indicate that growth occurs by the propagation of a stable planar liquid-solid interface. Under this mode of rapid

solidification, large elongated grains are formed, and the DP contains diffraction spots associated with grains close to a Bragg condition (Fig. 1c). In the RAI diffraction plots, {220} and {311} diffraction peaks start to develop on top of the diffuse background, which contains diffuse liquid Al and amorphous  $\text{Si}_3\text{N}_4$  intensities, indicating the simultaneous presence of liquid and crystalline solid Al (Fig. 1c). Tracing the progress of the solid-liquid interface during the transformation using the series of images, we determined that the interface is morphologically smooth, produces columnar grains, and moves with an estimated velocity of  $\sim 3\text{-}4$  m/s (Fig. 1). After solidification the DP showed a reduced diffuse background and distinct diffraction spots instead of diffraction rings, since the number of grains in the field of view was significantly reduced (Fig. 1d). The corresponding RAI plot is very similar to that of the as-deposited material (Fig. 1d). While Figure 1 contains a lot more information, its main purpose in this report is to demonstrate that the Al film was successfully molten inside the TEM and the progressing solid-liquid interface could be successfully traced during rapid solidification.

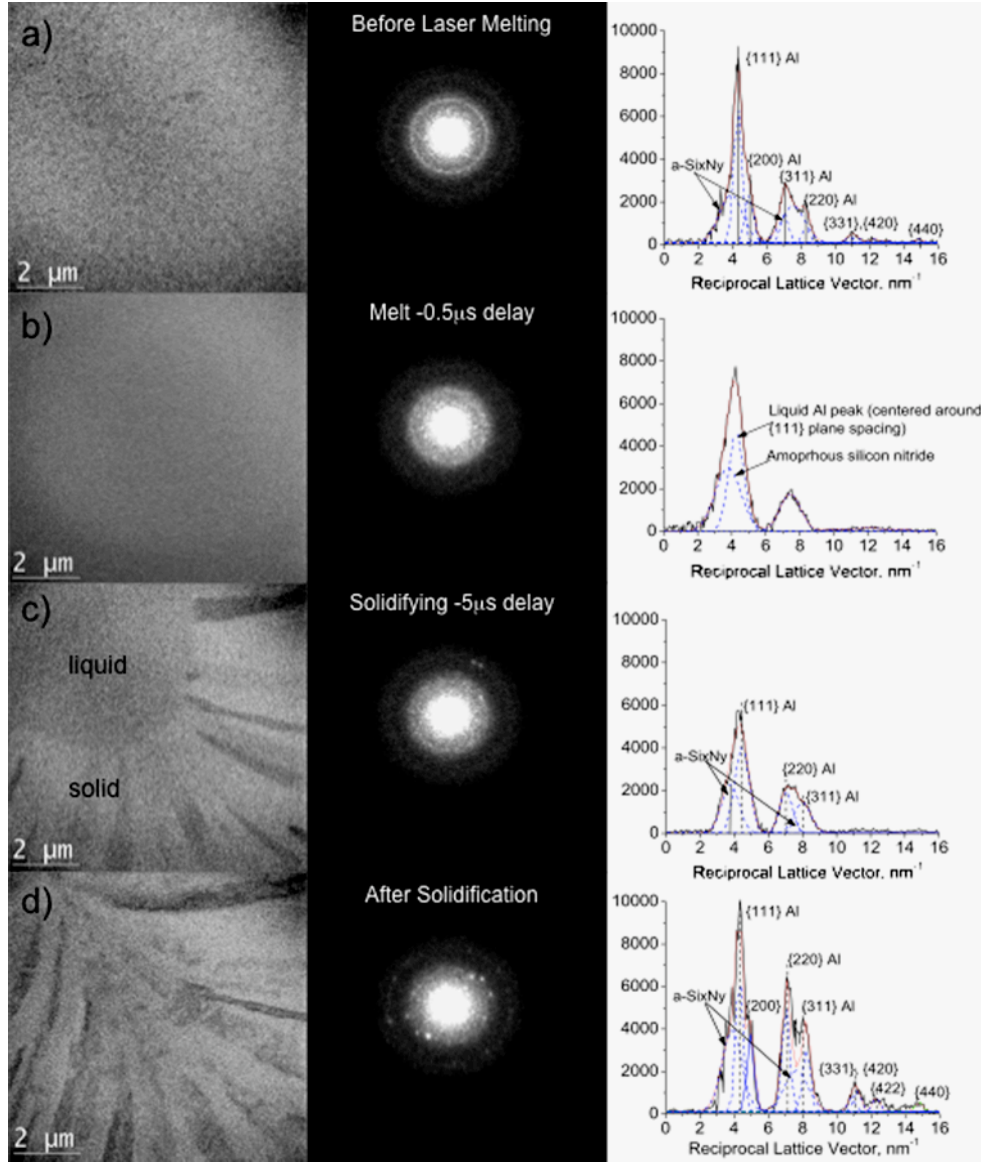


Figure 1: Time delay sequence of images, diffraction patterns and corresponding radial average intensity (RAI) vs. scattering angle (SA) plots taken a) before, with b) 0.5 $\mu$ s, c) 5 $\mu$ s time delays and d) after solidification is complete.

We used conventional TEM to analyze the re-solidified areas of the Al thin film (Fig. 2a-c and 2f). The rapidly solidified area contains large elongated grains stretching from the edge of the melt pool to its center (Fig. 2c and 2f). These grains are up to  $\sim 10 \mu\text{m}$  long,  $\sim 0.5\text{-}1.0 \mu\text{m}$  wide and  $0.08 \mu\text{m}$  thick (Fig. 2c). Bright field images (Fig. 2a) revealed the morphology of the grain boundaries between the elongated columnar grains as wavy and indistinct (Fig. 2a). Dark field imaging (Fig. 2b) revealed a very high concentration of defects in the grain interiors. Further analysis is required to determine the origin of the

unusual grain boundary structure and the defect content of the grains formed by rapid solidification.

We used automated acquisition and indexing of precession diffraction patterns in the TEM (ASTAR/DigiSTAR from NanoMEGAS [9]) to map grain orientations with a 10 nm step size on 1.5  $\mu\text{m}$  by 1.5  $\mu\text{m}$  area scans close to the original liquid solid interface prior to solidification (Fig. 2c-e). The orientations plotted in the montage of Fig. 2d, using the color code in Fig. 2e, are parallel to the solidification front growth direction. Based on the analysis of about 30 columnar grains no preferential growth direction could be identified, implying randomness in the growth direction selection, which would be consistent with solidification by rapid propagation of a stable, planar liquid-solid interface. We measured misorientation spreads within the elongated regions imaged by bright field TEM (Figs. 2a-c) of less than  $5^\circ$ , identifying them as single crystalline grains separated by general high angle grain boundaries. The orientation mapping in the TEM provided for robust identification of grains, grain boundary location, and grain boundary character with considerably improved lateral spatial resolution ( $\sim 10$  nm) compared to orientation imaging using scanning electron microscopes (SEM) [9].



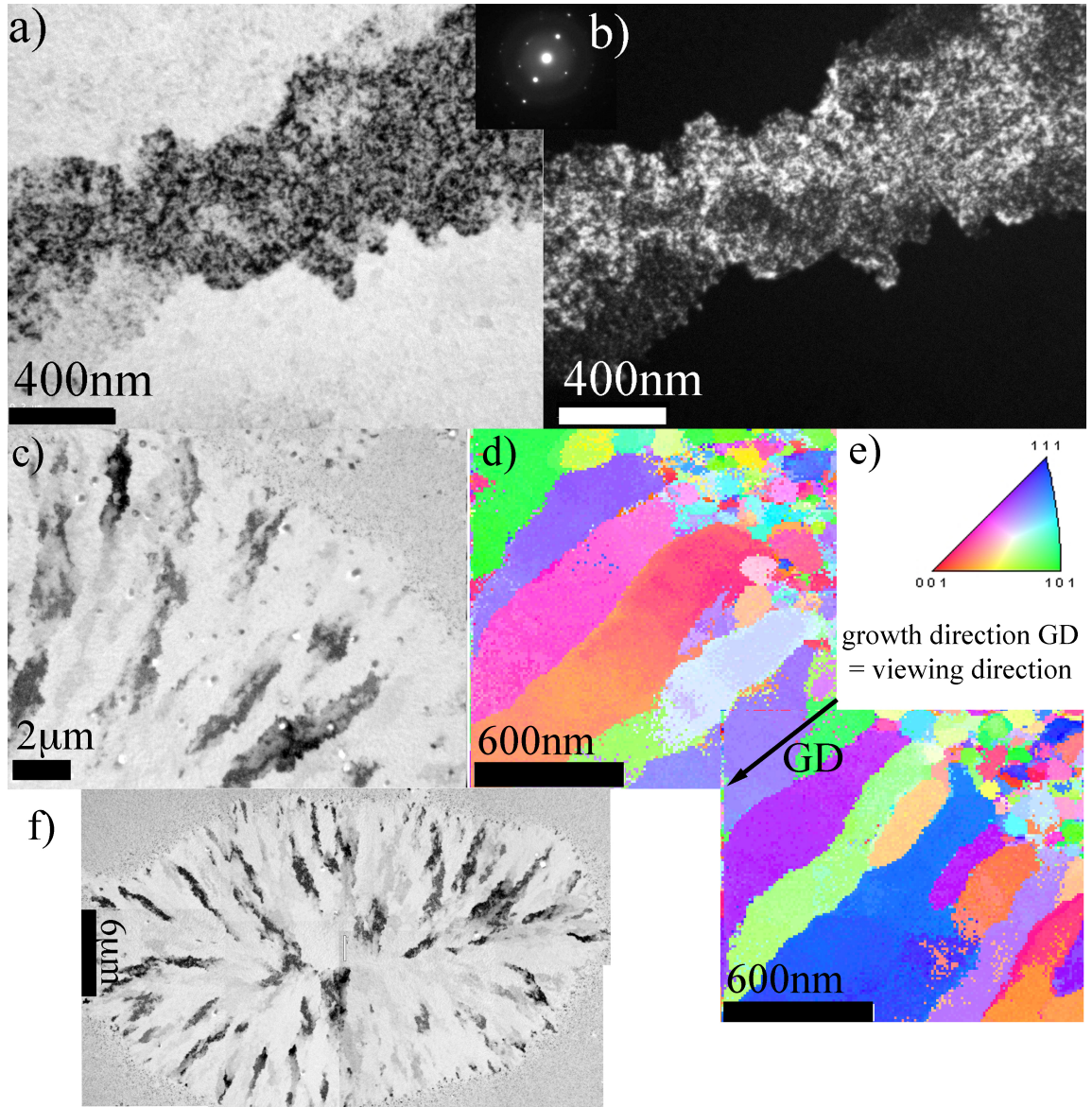


Figure 2: a) Multi - beam bright field image with inset diffraction pattern; b) corresponding dark field image using  $g = 111$ ; c) Bright field image of a rapidly solidified area analyzed with an automated orientation imaging system in the TEM; d) orientation maps looking along the growth direction; e) standard triangle orientation legend; f) illuminated spot after solidification

In summary, the combined spatial and temporal resolution of the DTEM permits the study of rapid solidification dynamics, quantification of solidification velocities, and observation of the morphology and crystallography of the solidifying microstructure in Al thin films. We determined that the liquid-solid interface is morphologically smooth during rapid solidification of Al thin films after pulsed laser melting and measured an interface

velocity of  $\sim 3 - 4$  m/s. Future plans include studying effects of interfacial velocity on microstructural morphology by controlled manipulation of the heat extraction and details of stability and morphology of the solid-liquid interface in solidification of solid solutions of thin metal films.

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